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**Supramolecular Assemblies and Redox Reactivities Regulated
by Hydrogen Bonding in Saddle-Distorted Porphyrins**
(サドル型ポルフィリンの水素結合による超分子形成挙動および酸化還元反応性の制御)

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| 主査 | 小島 隆彦 | 筑波大学 教授 | 工学博士 |
| 副査 | 山本 泰彦 | 筑波大学 教授 | Ph.D. |
| 副査 | 鍋島 達弥 | 筑波大学 教授 | 工学博士 |
| 副査 | 福住 俊一 | 名城大学 特任教授 | 工学博士 |

論 文 の 要 旨

In the doctoral thesis, the author described the rich redox properties and hydrogen-bonding abilities of saddle-distorted dodecaphenylporphyrin (**H₂DPP**) and its derivatives have been utilized to develop novel supramolecular assemblies, photoinduced supramolecular charge-separation systems, and metal-free redox catalytic systems.

In Chapter 1 as general introduction of this thesis, the author has surveyed the background of research described in this thesis, especially, chemistry of saddle-distorted porphyrins and the protonated derivatives. In Chapter 2, the author describes protonation behavior of **H₂DPP** by acids (HX) to control the thermodynamics in protonation of **H₂DPP** to form a monoprotinated **H₂DPP** (**H₃DPP⁺**) and diprotinated one (**H₄DPP²⁺**). **H₃DPP⁺** was stabilized by a hydrogen-bonding interaction of protic solvents such as MeOH, resulting in the selective formation of an unusual monoprotinated porphyrin. In addition, photodynamics of **H₃DPP⁺** was also explored by photoinduced intermolecular electron transfer from electron donors to the triplet excited state of **H₃DPP⁺** to determine the reorganization energy of electron transfer of **H₃DPP⁺**. In Chapter 3, the author clarified that thermodynamic stabilities of **H₄DPP²⁺** can be regulated by conjugate bases (X^-) of an acid (HX) used for the protonation: The weak hydrogen bonding between **H₄DPP²⁺** and X^- in **H₄DPP²⁺**(X^-)₂ destabilized **H₄DPP²⁺**(X^-)₂. Thus, in the presence of two kinds of conjugate bases (X^- and Y^-), the author successfully achieved selective formation of a supramolecular hetero-triad (**H₄DPP²⁺**(X^-)(Y^-)) in solution by using thermodynamically unstable **H₄DPP²⁺**(X^-)₂.

In Chapter 4, the author describes the formation of electron-transfer states in hydrogen-bonded supramolecular assemblies based on **H₄DPP²⁺** with redox-active molecules by femto-second laser-flash photolysis in deaerated acetone solutions. When a Ru(II) complex (**Ru^{II}COOH**) was employed to form **H₄DPP²⁺**(**Ru^{II}COO⁻**)₂, **H₄DPP²⁺** acted as an electron acceptor in photoinduced intrasupramolecular electron transfer to form one-electron reduced **H₄DPP²⁺** (**H₄DPP^{•+}**). On the other hand, in supramolecules of **H₄DPP²⁺** with a benzylviologen derivative (**BV²⁺COO⁻**), **H₄DPP^{•+}**,

formed through intermolecular electron transfer from ferrocene derivatives to $^3[\text{H}_4\text{DPP}^{2+}]^*$, which acts as an electron donor, indicating $\text{H}_4\text{DPP}^{2+}$ can function as an electron mediator in hydrogen-bonded supramolecular assemblies.

In Chapter 5, the author mentions the redox reactivity of multi-electron reduced porphyrinoids, which are formed by chemical reduction of $\text{H}_4\text{DPP}^{2+}$ derivatives. While two-electron reduced porphyrinoids (isophlorins) are usually unstable due to the contribution of 20π Hückel antiaromaticity, the author has achieved selective formation of an isophlorin derivative (**Iph**) by hydrogen-bonding stabilization of polar aprotic solvents with a saddle-distorted dodecaphenylisophlorin derivative. By using the stable isophlorin, further reduction of **Iph** afforded four-electron reduced porphyrinoids (**IphH₂**) showing unique reversible four-electron redox reactions involving **IphH₂** and the starting porphyrin. In addition, in Chapter 6, the author has presented thermodynamic stabilities of isophlorin derivatives by introducing methyl groups at inner nitrogen atoms. Especially *N*21, *N*23-dimethylated one (*syn*-**Me₂Iph**) and the corresponding porphyrin (*syn*-**Me₂P**) showed unprecedented redox reactivities; interconversion between O_2 and H_2O_2 has been achieved on the basis of reversible conversion between *syn*-**Me₂Iph** and *syn*-**Me₂P**. In the redox processes, two-point hydrogen bonding of *syn*-**Me₂P** (or *syn*-**Me₂Iph**) with H_2O_2 (or O_2) has been proposed to play a crucial role to establish the novel $\text{O}_2/\text{H}_2\text{O}_2$ interconversion. Furthermore, in Chapter 7, applying the robustness of the dimethylated isophlorin derivatives in the course of two-electron redox reactions, the author has constructed catalytic two-electron O_2 reduction systems in a metal-free manner. Under the catalytic conditions, the structural isomer of *syn*-**Me₂P** (*anti*-**Me₂P**) showed higher reactivity and selectivity in H_2O_2 production than those of *syn*-**Me₂P** and other metal-free catalysts previously reported. Hydrogen bonding between the isophlorin derivatives and O_2 has been also revealed to be indispensable for the high catalytic reactivity in H_2O_2 production.

Through this research, the author has established the utility of hydrogen bonding in formation of supramolecular assemblies and metal-free catalysts based on redox-active organic molecules such as porphyrins. Higher basicity of saddle-distorted porphyrins makes it possible to regulate the strength of hydrogen bonding by changing the chemical properties of conjugate bases of acids used for the protonation to form diprotonated porphyrins. The author describes selective formation of functional supramolecules such as hetero-triads by just controlling the strength of hydrogen bonding can provide a new strategy to develop useful hydrogen-bonded supramolecular assemblies as seen in Photosystem II. In addition, the author has explored the highly saddle-distorted structure of H_2DPP derivatives facilitates the protonation and selective formation of two-electron reduced species (isophlorins), which show high robustness and unique redox reactivities such as reversible four-electron reactions, $\text{O}_2/\text{H}_2\text{O}_2$ interconversion, and catalytic O_2 reduction reactions.

審 査 の 要 旨

〔批評〕

The contents of the doctor thesis are excellent and the parts of the thesis have been already published in high-impact academic journals including *Angew. Chem. Int. Ed.*, *Chem. Commun.*, and *Chem. Eur. J.*. Especially, the contents of Chapter 6, although they have yet to be published (under review at this moment), are surprising and outstanding: the author has established unprecedented $\text{H}_2\text{O}_2/\text{O}_2$ interconversion using a porphyrin/isophlorin redox couple without any metal ions. Based on the facts described in Chapter 6, the author presents the construction of catalytic dioxygen reduction using isophlorin derivatives as reactive reducing intermediates in Chapter 7; this demonstrates the utility of the porphyrinoids as organic catalysts to produce H_2O_2 as an energy source. In the catalytic H_2O_2 production, it should be noted that the author has clarified the difference of hydrogen-bonding mode of dioxygen causes the alteration of the reaction mechanisms as mentioned above. In Chapters 2 and 3, the author describes some requisites for the formation of monoprotonated porphyrins from viewpoint of thermodynamics. Also, the author has succeeded in the determination of the reorganization energy of electron transfer of a monoprotonated porphyrin for the first time. In Chapter 4, the author presents formation of supramolecular assemblies of $\text{H}_4\text{DPP}^{2+}$ with a Ru(II)-pyridylamine complex having 4-pyridine-carboxylate as a linker and also 4,4'-bipyridinium (viologen) derivatives having a carboxyl group as a hydrogen bonding site. Photodynamics has been clearly established for the photoinduced electron transfer from the hydrogen-bonded Ru(II) complex to $\text{H}_4\text{DPP}^{2+}$ and also from external electron donors to $\text{H}_4\text{DPP}^{2+}$ and successive thermal intrasupramolecular electron transfer from one-electron-reduced $\text{H}_4\text{DPP}^{\bullet+}$ to the hydrogen-bonded viologen derivative by means of laser flash photolysis. In Chapter 5, the author has presented the formation and crystal structure determination of a novel and interesting four-electron-reduced species of a diprotonated saddle-distorted porphyrin formed through two-electron reduction of the corresponding isophlorin. The author also demonstrated a novel function of diprotonated porphyrin as an electron mediator in photoinduced electron transfer.

All reviewers of this thesis have recognized the quality and excellence of the achievements described in this thesis.

In summary, in the light of the quality and significance of the contents, this doctor thesis provided by the author should be acceptable.

〔最終試験結果〕

The final examination committee conducted the fi defense seminar on February 13, 2019. The applicant provided an overview of dissertation, addressed questions and comments raised during Q&A session. All of the committee members reached a final decision that the applicant has passed the final examination.

[結論]

Based on the results of the above-mentioned dissertation defense and final examination, the final examination committee approved that the applicant is qualified to be awarded Doctor of Philosophy in Science.